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Patents Form 1/77

Patent 1977

**The
Patent
Office**25 JUL 03 182473 1 D02700
P01/770 0.00 0317208.7**1/77****Request for grant of a patent**

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23 JUL 2003

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1. Your reference **CDK2124**
2. Patent application number
(The Patent Office will fill in this part) **0317208.7**
3. Full name, address and postcode of the or of
each applicant (underline all surnames) **23 JUL 2003**
RHODIA CONSUMER SPECIALTIES LIMITED
Oak House, Reeds Crescent, Watford,
Hertfordshire, WD24 4QP,
- Patents ADP number (if you know it) **7870322006**
- If the applicant is a corporate body, give the
country/state of its incorporation **England**
4. Title of the invention **SCALE INHIBITION IN WATER SYSTEMS**
5. Name of your agent (if you have one) **Barker Brettell**
"Address for service" in the United Kingdom
to which all correspondence should be sent
(including the postcode) **138 Hagley Road**
Edgbaston
Birmingham
B16 9PW
- Patents ADP number (if you know it) **7442494002**
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and the date of filing of the or of each of these
earlier applications and (if you know it) the or
each application number
- | Country | Priority application number
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7. If this application is divided or otherwise
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8. Is a statement of inventorship and of right to
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request (Answer 'Yes' if:
a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant,
or
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See note (d)) **YES**

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Continuation sheets of this form -

Description 8 + 8

Claim(s) 3 + 3

Abstract -

Drawing(s) 1 + 1

10. If you are also filing any of the following, state how many against each item.

Priority documents -

Translations of priority documents -

Statement of inventorship and right to grant of a patent (*Patents Form 7/77*) -

Request for preliminary examination 1
(*Patents Form 9/77*)

Request for substantive examination -
(*Patents Form 10/77*)

Any other documents -
(*please specify*)

11. I/We request the grant of a patent on the basis of this application.

Signature

Barker Brettell
Barker Brettell

Date

22 July 2003

12. Name and daytime telephone number of person to contact in the United Kingdom

Colin D. Kinton

Tel: 0121 456 1364

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Patents Form 1/77

SCALE INHIBITION IN WATER SYSTEMS

This invention relates to scale inhibition in water systems.

5 In particular, the present invention relates to a composition for inhibiting the formation of scale in water systems (especially systems where the fluids are exposed to a range of temperatures, e.g. in hydrocarbon production, where temperatures are high at a sub-sea wellhead and reduce as the fluids travel to the production facility along a sub-sea tie-line). Conventionally,
10 scale inhibitors tend to function well either at high or low temperatures, but not both.

We also claim a method for inhibiting the formation of scale in water systems by means of such a composition, to a water system so treated and
15 to the use of such a composition for the inhibition of scale (especially barium sulphate scale) in a water system.

At the wellhead, fluids can often be at 100°C or more whereas, along the tie-line, the temperature can reduce to as little as 5°C before the fluids
20 reach the production facility.

It is therefore vital to ensure that effective scale control is provided over the whole temperature range to which the fluids are exposed, particularly for sub-sea wells (including deepwater applications) with long tie-backs.
25 Here, produced fluids typically travel around many tens of km along the sea-bed and in such applications, the costs of intervention, should scale occur, are high.

Previous technology has involved the use of scale inhibitors, such as
30 phosphonates (which are maximally effective at high temperatures) and sulphonated polymers (which are maximally effective at low temperatures)

but, hitherto, scale inhibitors which are fully effective at both low and high temperatures have not been available.

We have now unexpectedly found that copolymers or terpolymers
5 containing both phosphonate and sulphonate groups (with the addition in
terpolymers, of carboxylate groups) can produce enhanced scale-inhibition
in water systems over a range of temperatures.

In a first aspect, therefore, the present invention provides a composition for
10 inhibiting the formation of scale in a water system at both wellhead and
seabed temperatures, the composition comprising:

(a) a copolymer of an unsaturated phosphonic acid (or salt of such an acid)
with an unsaturated sulphonic acid (or salt of such an acid) or an
15 unsaturated carboxylic acid (or salt of such an acid)

or

(b) a terpolymer of an unsaturated phosphonic acid (or salt of such an acid)
with an unsaturated sulphonic acid (or salt of such an acid) and an
unsaturated carboxylic acid (or salt of such an acid).

20

Examples of suitable unsaturated phosphonic acids include
vinylphosphonic acid (VPA) (or a salt thereof) and vinylidene-1,1-
diphosphonic acid (VDPA) (or a salt thereof).

25 Examples of suitable unsaturated sulphonic acids include vinylsulphonic
acid (VSA) (or a salt thereof), and AMPS(2-acrylamido-2-methylpropane
sulphonic acid) (or a salt thereof) .

Examples of suitable unsaturated carboxylic acids include acrylic acid
30 (AA) (or a salt thereof) and methacrylic acid (MAA) (or a salt thereof).

Accordingly, the composition according to the first aspect of the present invention may comprise any of the following:

- 5 (i) a copolymer of VPA (or a salt thereof) and VSA (or a salt thereof),
an especially-preferred copolymer being a 1:20 copolymer of VPA
and VSA;
- (ii) a copolymer of VPA (or salt thereof) and AA or MAA (or salt
thereof)
- 10 (iii) a copolymer of VDPA (or a salt thereof) and AA (or a salt thereof)
or MAA (or a salt thereof);
- (iv) a copolymer of VDPA (or a salt thereof) and VSA (or a salt thereof)
- 15 (v) a terpolymer of VPA (or a salt thereof), AA (or a salt thereof) and
VSA (or a salt thereof);
- (vi) a terpolymer of VPA (or a salt thereof), MAA (or a salt thereof) and
20 VSA (or a salt thereof);
- (vii) a terpolymer of VDPA (or a salt thereof), AA (or a salt thereof) and
VSA (or a salt thereof);
- 25 (viii) a terpolymer of VDPA (or a salt thereof), MAA (or a salt thereof)
and VSA (or a salt thereof).

Where a salt of an unsaturated phosphonic, sulphonic or carboxylic acid is
used, the salt may be a wholly-neutralised or partially-neutralised salt (for
30 example a wholly- or partially-neutralised sodium, potassium or ammonium
salt of the unsaturated acid).

In a second aspect, the present invention provides a method for inhibiting the formation of scale in a water system operating at high (e.g. wellhead) and low (e.g. seabed) temperatures, the method comprising the addition to the water system of a scale inhibiting amount of a composition according to

5 the first aspect of the present invention hereinabove described.

Suitably, the composition is added to the water system in an amount of up to 1000 ppm, more typically 1- 200 ppm.

10 Generally, for sub-sea applications, the seabed temperature of the water system is about 5 degrees Celsius and the wellhead temperature can be up to 200 degrees Celsius.

In a third aspect, the present invention provides a water system treated by
15 the method according to the second aspect of the present invention hereinabove described.

Suitably, the water system so treated is operatively associated with an
oilfield or an oil-well. Application may be by injection of the scale
20 inhibitor into the fluid stream by means of, e.g. a dosing pump but often, application is by "squeeze" treatment whereby the scale inhibitor is forced into the oil bearing formation from whence, subsequently, it bleeds back slowly into the produced fluids thus treating them at the appropriate level to inhibit scale.

25

In a fourth aspect, the present invention provides the use in a water system of a composition according to the first aspect of the present invention hereinabove described, to inhibit the formation of scale at seabed
temperatures.

30

In particular, the scale is barium sulphate scale.

The invention will be illustrated, in a preferred embodiment, by way of the following Examples.

METHODOLOGY

5

The standard static 'breaker' sulphate scale inhibition test described in the Heriot Watt FAST 'Experimental Procedure Manual' Version 2.0 was followed.

10 Tested inhibitors are detailed in Table 1 (below):

TABLE 1

| Inhibitor Functionality | Available as |
|---|--------------------------|
| VSA homopolymer | MIRAPOL®6720 |
| diethylene triamine pentakis(methylene phosphonic acid), 45% aqueous solution of sodium salt | BRIQUEST®543-45AS |
| phosphonate end-capped poly(acrylic acid) | AQUARITE®EC4020 |
| phosphonate end-capped VSA/AA copolymer | AQUARITE®ESL |
| VPA/VSA random copolymer | AQUARITE®ES1027 |
| AA/MAA/VSA random copolymer | BEVALOID®6785 |

15 Test brines were North Sea seawater and a medium-scaling formation water (Nelson). Brine formulations are given in Table 2 below. Brines were mixed in a 50:50 ratio. All brines were buffered to pH = 5.5 using a sodium acetate/acetic acid buffer (34g of sodium acetate tri-hydrate and

0.75g of concentrated acetic acid, made up to 250ml in a volumetric flask with distilled water). All brines were filtered through a $0.45\mu\text{m}$ filter before use (to remove potential nucleation sites).

5

TABLE 2

Composition of brines used in
static barium sulphate inhibition efficiency tests

| salt | seawater g/l | Nelson formation water g/l |
|---|-----------------|-------------------------------|
| NaCl | 24.41 | 79.50 |
| $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ | 2.34 | 10.93 |
| $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ | 11.44 | 6.18 |
| KCl | 0.877 | 1.25 |
| $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ | - | 0.48 |
| $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ | - | 2.35 |
| Na_2SO_4 | 3.98 | - |

- 10 Inhibitor stock solutions of 1000ppm (in seawater) were diluted to give 20ppm, 30ppm and 40ppm stocks in seawater. Two aliquots of 100mls of each stock were placed in two 100ml Azlon® plastic bottles (test in duplicate). Two sets of blanks were also prepared containing seawater (minimum barium blank) and distilled water (maximum barium blank).
- 15 Into an equivalent number of 250ml Azlon® bottles were placed 100mls of formation water and 2mls of buffer. All seawater bottles were placed in a refrigerator at 5°C and all formation water bottles were placed in a pre-cooled water bath at 5°C . Bottles were kept for 2 hours at that temperature. The seawater was then added to the formation water and the bottles
- 20 replaced in the water bath at 5°C . This gave final inhibitor test doses of 5, 10 and 15ppm inhibitor. Bottles were sampled after 2 and 22 hours. These sampling times represent scale inhibition by nucleation inhibition and

crystal growth inhibition mechanisms respectively. A 1ml sample was taken from each bottle (taking care not to pick up any deposited scale). This was injected into a plastics test tube containing 9mls of a pre-prepared quench solution (28.559g of KCl, 5g of ScaleTreat®810 PVS in distilled water, adjusted to pH + 8.0 – 8.5 with NaOH and made up to 5 litres in a 5 litre volumetric flask). Each sample was analysed for residual barium by ICP analysis.

The barium sulphate inhibition efficiency was then calculated as follows:

$$\% \text{ efficiency} = \frac{[\text{Ba}^{2+} \text{ in sample}] - [\text{Ba}^{2+}]_{\min}}{[\text{Ba}^{2+}]_{\max} - [\text{Ba}^{2+}]_{\min}} \times 100$$

$[\text{Ba}^{2+}]_{\max}$ = Ba^{2+} content of maximum (FW/H₂O)blank

$[\text{Ba}^{2+}]_{\min}$ = Ba^{2+} content of minimum (FW/SW)blank

The results are shown in tabular form in Table 3 (below) and in graphical form in the accompanying drawing.

20

TABLE 3

| Inhibitor | % Ba efficiency | | | | | |
|-------------------|-----------------|-------|-------|----------|-------|-------|
| | 2 hours | | | 22 hours | | |
| | 5ppm | 10ppm | 15ppm | 5ppm | 10ppm | 15ppm |
| MIRAPOL®6720 | 41 | 53 | 81 | 6 | 14 | 24 |
| BEVALOID®6785 | 33 | 65 | 90 | 11 | 16 | 25 |
| BRIQUEST®543-45AS | 30 | 24 | 16 | 2 | 2 | 1 |
| AQUARITE®EC4020 | 28 | 69 | 78 | 10 | 19 | 25 |
| AQUARITE®ES1027 | 65 | 92 | 104 | 15 | 33 | 55 |
| AQUARITE®ESL | 21 | 59 | 77 | 11 | 22 | 39 |

The results show the enhanced scale inhibiting properties of a copolymer of VPA and VSA in comparison with other sulphonate polymers.

CLAIMS

1. A composition for inhibiting the formation of scale in a water system operating at both high and low temperatures, such as wellhead and seabed temperatures encountered during sub-sea production of hydrocarbons, the composition comprising:
 - (a) a copolymer of an unsaturated phosphonic acid (or salt of such an acid) with an unsaturated sulphonic acid (or salt of such an acid) or an unsaturated carboxylic acid (or salt of such an acid);
 - or
 - (b) a terpolymer of an unsaturated phosphonic acid (or salt of such an acid) with an unsaturated sulphonic acid (or salt of such an acid) and an unsaturated carboxylic acid (or salt of such an acid).
2. A composition according to Claim 1, comprising a copolymer of vinylphosphonic acid (VPA) (or a salt thereof) and vinylsulphonic acid (VSA) (or a salt thereof).
3. A composition according to Claim 1 or 2, comprising a 1 : 20 copolymer of VPA and VSA.
4. A composition according to Claim 1, comprising a copolymer of VPA (or a salt thereof) and acrylic acid (AA) (or a salt thereof) or methacrylic acid (MAA) (or a salt thereof).
5. A composition according to Claim 1, comprising a copolymer of vinylidene-1,1-diphosphonic acid (VDPA) (or a salt thereof) and AA (or a salt thereof) or MAA (or a salt thereof).
6. A copolymer of VDPA (or a salt thereof) and VSA (or a salt thereof)

7. A composition according to Claim 1, comprising a terpolymer of VPA (or a salt thereof), AA (or a salt thereof) and VSA (or a salt thereof).

8. A composition according to Claim 1, comprising a terpolymer of
5 VPA (or a salt thereof), MAA (or a salt thereof) and VSA (or a salt thereof).

9. A composition according to Claim 1, comprising a terpolymer of
10 VDPA (or a salt thereof), AA (or a salt thereof) and VSA (or a salt thereof).

10. A composition according to Claim 1, comprising a terpolymer of
VDPA (or a salt thereof), MAA (or a salt thereof) and VSA (or a salt thereof).

15

11. A composition according to any one of the preceding claims, in which the salt of the phosphonic acid, sulphonic acid or carboxylic acid is a wholly-neutralised or partially-neutralised salt.

20 12. A composition according to Claim 11, in which the salt is a sodium salt, a potassium salt or an ammonium salt.

13. A method of inhibiting the formation of scale in a water system at wellhead and seabed temperatures, the method comprising the addition to
25 the water system of a scale inhibiting amount of a composition according to any one of the preceding claims.

14. A method according to Claim 13, in which the composition is added to the water system in an amount of up to 1000 ppm.

30

15. A method according to Claim 14, in which the composition is added to the water system in an amount of from 1 ppm to 200 ppm.

16. A method of inhibiting the formation of scale in a water system, substantially as hereinbefore described with reference to the Examples.

5 17. A method according to any one of Claims 13 to 16, in which the system water temperature at the wellhead is in the range 80-200°C and the seabed temperature, is about 5 degrees Celsius.

18. A water system treated by the method of any one of Claims 13 to 17.

10

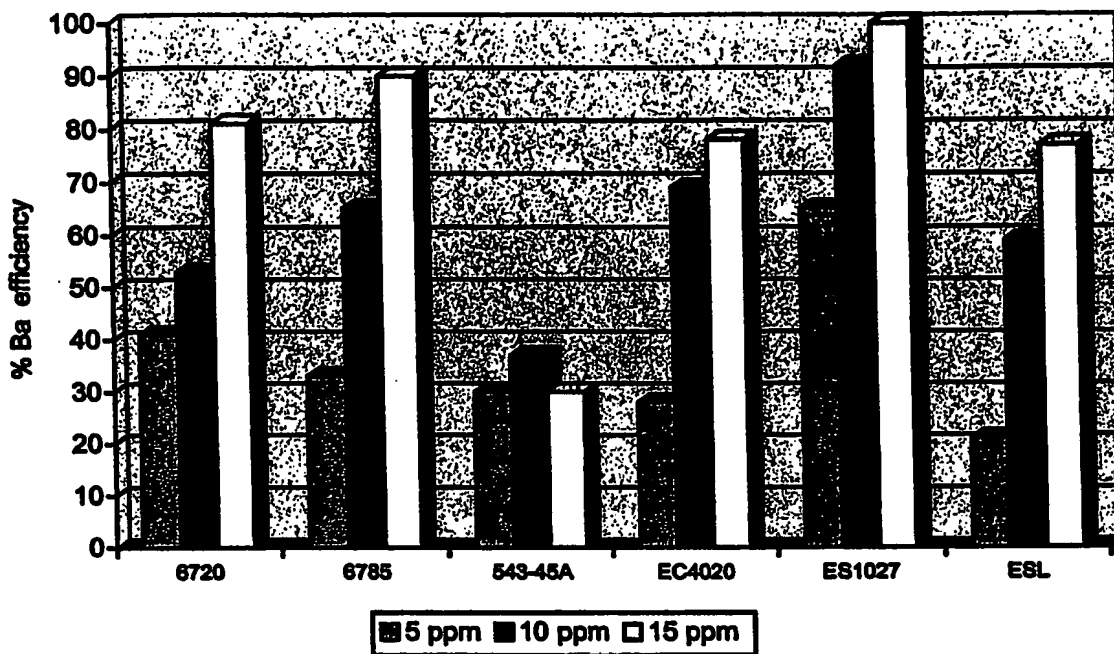
19. A water system according to Claim 18, which is operatively associated with an oilfield or oil-well.

20. The use in a water system of a composition according to any one of
15 Claims 1 to 12 to inhibit the formation of scale at high (e.g. wellhead) and low (e.g. seabed) temperatures.

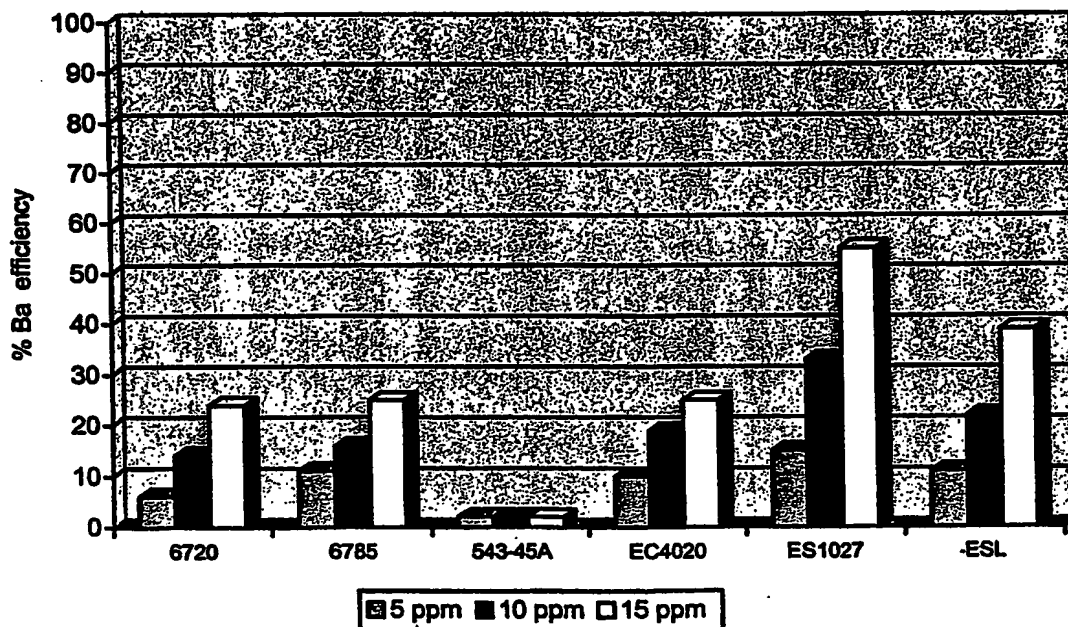
21. The use according to Claim 20, in which the scale is barium sulphate scale.

20

Barium sulphate inhibition efficiencies after 2hrs
50 Nelson Forties FW (2,000ppm Ca²⁺) : 50 SW @ 5°C



Barium sulphate inhibition efficiencies after 22hrs
50 Nelson Forties FW (2,000ppm Ca²⁺) : 50 SW @ 5°C



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